Elevated Pressure Adsorption of Methane on Activated Carbon;
Effects of Contaminant Gases and Repeated Cycling

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## INTRODUCTION

Bureau of Mines interest in methane adsorption was developed from re-
search on hydrogasification of coal to produce synthetic pipeline gas. The
product from hydrogasification consists principally of methane and hydro-
gen[2,6] the methane content varying from 5 to 80 percent depending on
process variables. The minor constituents are nitrogen, carbon oxides,
sulfur compounds, unsaturates, higher molecular weight hydrocarbons including
aromatics, and water vapor. Synthetic pipeline gas with a heating value of
approximately 1,000 Btu's can be produced from hydrogasification product by
recovering the methane. The Bureau of Mines has reported that estimated
capital and operating costs for separating methane from mixtures of methane
and hydrogen are lowest if the methane is adsorbed by activated carbon[8].
The estimate, however, was based on extrapolated data[5] for the adsorption
of pure methane at relatively low pressures. The objective of this in-
vestigation was to establish adsorption isotherms for methane on activated
carbon at 40° C and pressures of 14.2 to 800 psia and study the tendency of
activated carbon to lose its adsorptive capacity for methane when the methane
is contaminated with other gases and/or there is repeated cycling.

Effects of adding benzene, hydrogen, ethylene, or hydrogen sulfide were
investigated. These gases were chosen as contaminants because they are in the
gaseous mixture produced by hydrogasification. Two of the contaminant gases,
benzene and hydrogen, used in the experiments were given concentrations simi-
lar to those found in a hydrogasification product. The other two contaminants,
ethylene and hydrogen sulfide, were given much higher concentrations than
would be found in a hydrogasification product in order to simulate rapid
poisoning of the adsorbent.

The adsorptive capacity of activated carbon can be affected by side re-
actions. Activated carbon may act catalytically to convert hydrogen sulfide
to free sulfur in the presence of trace amounts of oxygen, and the free sulfur
may occupy space that could be taken up by the methane.[1]

## APPARATUS AND PROCEDURE

Some of the main components of the fixed-bed adsorption unit are shown in figure 1. The adsorber was made of type 304 stainless steel as were the valves, fittings, tubing, and gas collection reservoirs, because of their contact with hydrogen sulfide. The adsorber was 24 inches long with 1/2-inch outside diameter and 3/8-inch inside diameter. It had a maximum working pressure of 1,500 psi and a maximum working temperature of 450° C. During desorption, heat was supplied electrically using the adsorber wall as an electrical resistor. Power for heating was supplied by a 7.5 KVA, 10:1 step-down transformer. During the cooling cycle, the adsorber was rapidly cooled along its entire length by air blown from a series of small nozzles.

During the rapid cycling studies, the adsorption, desorption, and cooling cycles were automatically controlled by a time cycle controller. A complete cycle consisted of a 9-minute adsorption period at 40° C, 6 minutes desorption at 450° C, and 3 minutes cooling.

Figure 2 is a schematic flow diagram of the rapid cycling, fixed-bed adsorption system. The desired feed gas of known composition is supplied to the unit from high-pressure storage cylinders. The gas flow rate is measured by pressure drop through a calibrated capillary manometer. The gas saturator was used to add benzene to the feed gas when the contaminating effect of benzene was studied.

A weighed sample of fresh activated carbon was placed in the adsorber prior to each series of experiments. The activated carbon was degassed under vacuum for 2 to 3 hours at 450° C. At the end of this period the pressure in the adsorption chamber, measured by a McLeod gage, was about 15 microns Hg. The "dead space" in the reactor system was the volume of the adsorption chamber bounded by three solenoid valves, SV-1, SV-2, and SV-3. It represented the adsorbent pore volume, the interparticle void space, plus the volume of the apparatus capillary lines inside the respective boundaries. Dead space was determined by introducing measured amounts of helium at atmospheric pressure into the evacuated adsorption chamber, noting the equilibrium pressure, and applying the ideal gas law. Adsorption of helium was assumed to be negligible under these conditions.

In determining the amount of methane adsorbed for the pure methane experiments (static studies), methane was fed into the adsorption chamber until equilibrium conditions were attained. Equilibrium was attained rapidly, in some cases within 15 minutes. The gas was then desorbed from the adsorption chamber into a 500-cc calibrated collection reservoir. The desorption temperature was 450° C for all the experiments. A slow helium purge was also used in conjunction with the high temperature to remove the last traces of methane. The amount of methane adsorbed on the activated carbon was the difference between the total methane collected and that contained in the dead space.

In the mixture experiments (dynamic studies), it was assumed that methane equilibrium was attained in approximately the same length of time required during the pure methane experiments (static studies). After methane equilibrium was attained, the gas remaining in the dead space and on activated carbon's surface was desorbed into the 500-cc calibrated collection reservoir. The amount of methane adsorbed was determined in a manner similar to that used for the static studies.

The ideal gas law was used for computing the amount of adsorbed gas when the total adsorption pressure did not exceed 50 psi. Generalized compressibility factors[9] were used in conjunction with Amagat's law when total pressure exceeded 50 psi.

All gases were analyzed by chromatography and mass spectrometry. The methane used in the experiments contained 0.2 percent ethane and 0.1 percent nitrogen. The adsorbent was a 12x30 mesh Pittsburgh Coke and Chemical Co. Type BPL activated carbon manufactured from various grades of bituminous coal combined with suitable binders.

## RESULTS AND DISCUSSION

When adsorption takes place in a unimolecular layer, or part of a layer, the data can often be fitted satisfactorily by means of the simple Langmuir equation[7]

$$x/m = \frac{a\,b\,P}{1 + a\,P}.$$

In this formula

    x  = weight of gas adsorbed.
    m  = weight of solid adsorbent.
    P  = Partial pressure of the gas in question at equilibrium.
    a, b = experimental constants.

The Langmuir equation is based on the assumption that the molecules of the adsorbed gas are present on the surface of the adsorbent as a monolayer. The greater the fraction of the surface covered by the monolayer, the less tendency there is to accumulate more molecules and the greater the partial pressure must be to continue such accumulation.

The Langmuir formula may be rewritten as the equation of a straight line,

$$P/(x/m) = (1/b)\,P + 1/(a\,b).$$

The experimental constants a and b can be calculated if the plot of $P/(x/m)$ versus P is a straight line. Figure 3 shows Langmuir plots of our experimental data and data of four other investigators, Per K. Frolich[4],

L. Szepesy[11], G. C. Ray[10], and R. J. Grant[5]. Curve 5 represents Grant's extrapolated data. These extrapolated data were used in our original cost estimates.

Plots of both Szepesy's and our data, curves 2 and 3, produced straight lines. The upper portion of Frolich's data, curve 1, is also a straight line. The experimental constants for curves 2 and 3 become:

  1) Curve 2:   a = 9.64x10$^{-3}$ psia$^{-1}$, b = 7.41 g/100 g.

  2) Curve 3:   a = 12.85x10$^{-3}$ psia$^{-1}$, b = 5.56 g/100 g.

Freundlich's equation, $x/m = a\ P^{1/n}$ [3], is used frequently to correlate adsorption data. The letters x, m, and P have the same meaning as in the Langmuir equation, and the letters a and 1/n represent empirical constants.

The validity of the formula for the experimental data can be tested by plotting the logarithm of x/m against the logarithm of P, since rewriting the formula in its logarithm form, log (x/m) = log a + (1/n) log P, gives the equation of a straight line.

Figure 4 shows Freundlich plots of our experimental data and data of the four other investigators previously mentioned. None of the curves obeys the Freundlich equation.

Table 1 shows the effect of 76.5 percent hydrogen in the methane feed gas upon activated carbon's adsorptive capacity for methane. In these series of experiments, two methane partial pressure levels were investigated, 50 and 300 psia. Activated carbon's equilibrium capacity for methane was reduced 10.0 and 22.8 percent, respectively, owing to the presence of hydrogen. Experiments with a methane-hydrogen mixture showed that the selectivity of the carbon for methane over hydrogen was 11:1 at 50 psia partial pressure, and 28:1 at 300 psia.

Figure 5 shows the effect of methane contamination and repeated cycling upon activated carbon's adsorptive capacity of methane. Benzene, hydrogen, ethylene, and hydrogen sulfide were the contaminants tested. After the first adsorption step, all the contaminants reduced the capacity of activated carbon for methane. The initial reductions in capacity for methane owing to the presence of the contaminants are given in percent in table 2. The presence of 8.3 percent hydrogen sulfide produced the greatest initial loss of capacity, reducing the carbon's capacity for methane by 53 percent. Benzene, hydrogen, and ethylene reduced the methane capacity of the carbon by 13, 25, and 37 percent, respectively.

Additional adsorption-desorption cycles using the contaminated methane feed gases incurred no further decrease in carbon capacity for methane except in the tests using 10.3 percent ethylene in the methane feed gas. After 150 cycles, activated carbon's capacity for methane was reduced an additional 13 percent from 37 to 50 percent.

TABLE 1.- Effect of hydrogen upon activated carbon's
adsorptive capacity for methane

| Feed gas | Adsorption temperatures, °C | equilibrium pressure, psia | Activated carbon's capacity for methane, g CH₄ 100 g carbon | Activated carbon's capacity for hydrogen, g H₂ 100 g carbon | Selectivity, Carbon capacity($CH_4$) Carbon capacity($H_2$) |
|---|---|---|---|---|---|
| a) $CH_4$ [1] | 40 | 50 | 2.49 | -- | -- |
| b) 23.7 pct $CH_4$ + 76.3 pct $H_2$ | 40 | 50 | 2.24 | 0.02 | 11:1 |
| a) $CH_4$ [1] | 40 | 300 | 5.49 | -- | -- |
| b) 23.7 pct $CH_4$ + 76.3 pct $H_2$ | 40 | 300 | 4.23 | 0.15 | 28:1 |

[1] Containing 0.2 pct $C_2H_6$ and 0.1 pct $N_2$.

TABLE 2.- Reduction in activated carbon's capacity for methane by
contaminating gases and repeated cycling [1]

| Contaminating gas, vol-pct | Percent | | |
|---|---|---|---|
| | Initial reduction in capacity for methane (without recycling) | Reduction in capacity for methane after 150 cycles | Saturation of activated carbon with impurity |
| 0.35 $C_6H_6$ | 13.0 | 14.0 | 10.0 |
| 76.3 $H_2$ | 25.0 | 25.0 | 100.0 |
| 10.3 $C_2H_4$ | 37.0 | 50.0 | 75.0 |
| 8.3 $H_2S$ | 53.0 | 53.0 | 100.0 |

[1] Conditions: Adsorption temperature 40° C; Methane equilibrium presure 300 psia.

In these contaminating and cycling tests, hydrogen and hydrogen sulfide were the only two contaminants that completely saturated the activated carbon. Benzene and ethylene only reached 10 and 75 percent carbon saturation, respectively. In all of the tests conducted, methane attained equilibrium conditions or 100 percent saturation before desorption was initiated. Degree of saturation was determined through adsorber tail gas analyses.

Experiments were conducted about five times for each pure methane equilibrium point. Standard deviation from the mean value was ± 1-2 percent for these experiments. Standard deviation for the methane-hydrogen mixture experiments conducted at the two partial pressure levels was ± 15 percent. Greater scattering of data occurred when the small quantities of hydrogen adsorbed were being determined.

## CONCLUSIONS

1. Increased total pressure favors the preferential adsorption of methane from methane-hydrogen mixtures. However, methane is less strongly adsorbed from the mixture than when it is present at the same partial pressure in the pure state. Lower values for methane adsorption at high partial pressures were found experimentally than those extrapolated from existing data at lower pressures.

2. Each impurity of hydrogasification product gas tested decreased activated carbon's capacity for methane. Although the carbon was not completely saturated with benzene and ethylene, these impurities still contributed significantly to the initial lowering of the adsorbent's capacity for methane.

3. Repeated cycling, up to 150 cycles, in the presence of the contaminants did not further decrease activated carbon's capacity for methane except when ethylene was added.

4. These results indicate that the cost estimates reported earlier[8/] were too low because the extrapolated values for methane adsorption were too high. The efficiency of activated carbon in adsorbing methane is lowered by other gases mixed with the methane and, when ethylene is present, by repeated cycling. However, for most of the cases of separation investigated ($CH_4$ concentrations of 5, 20 and 50 pct), the economics of adsorption by activated carbon are now considered to be approximately the same as separation by liquefaction of methane.

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11. Szepesy, L., and V. Illes. Adsorption of Gases and Gas Mixtures. Acta Chim. Hung. Tomus., v. 35, 1963, pp. 37-50; 53-59.
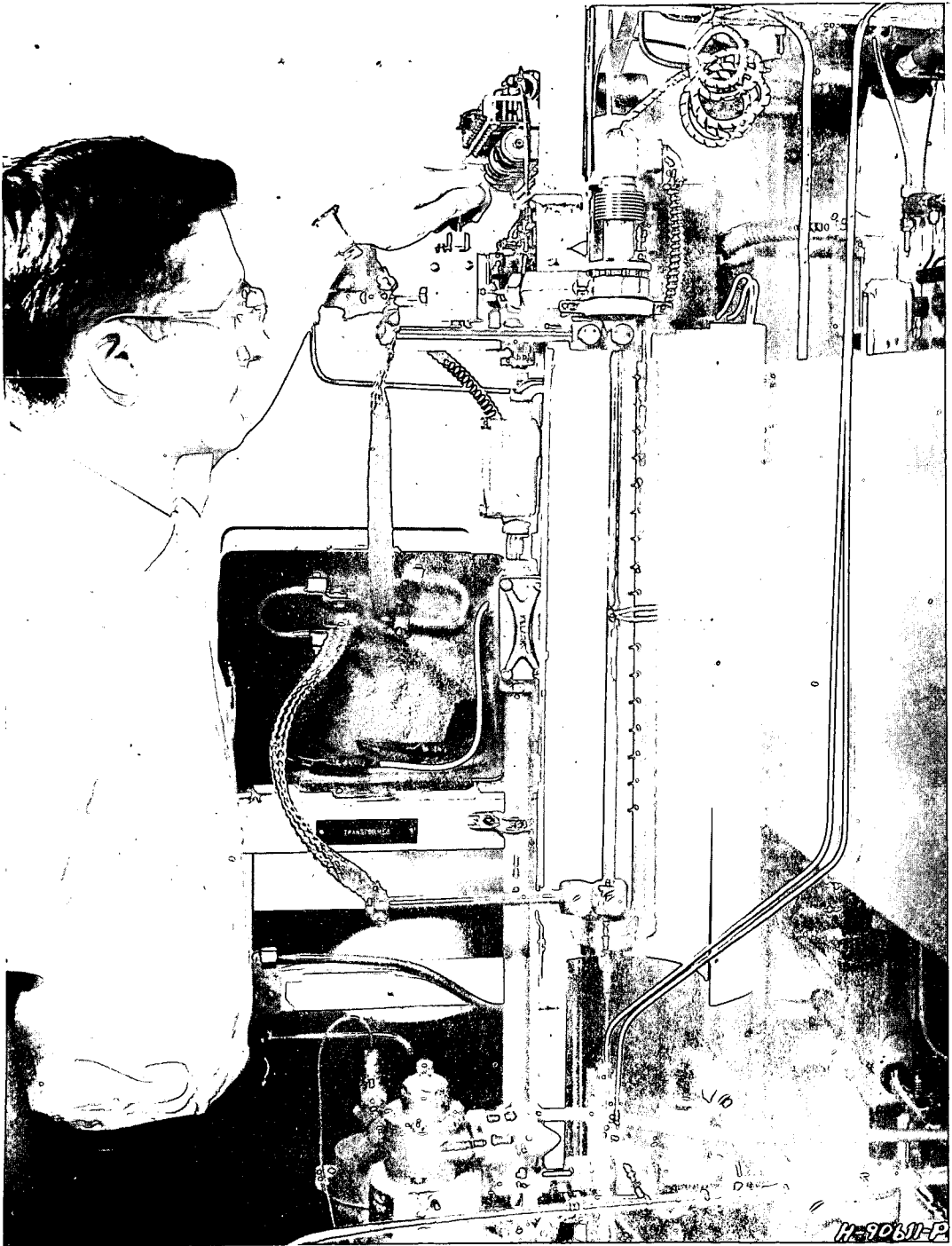
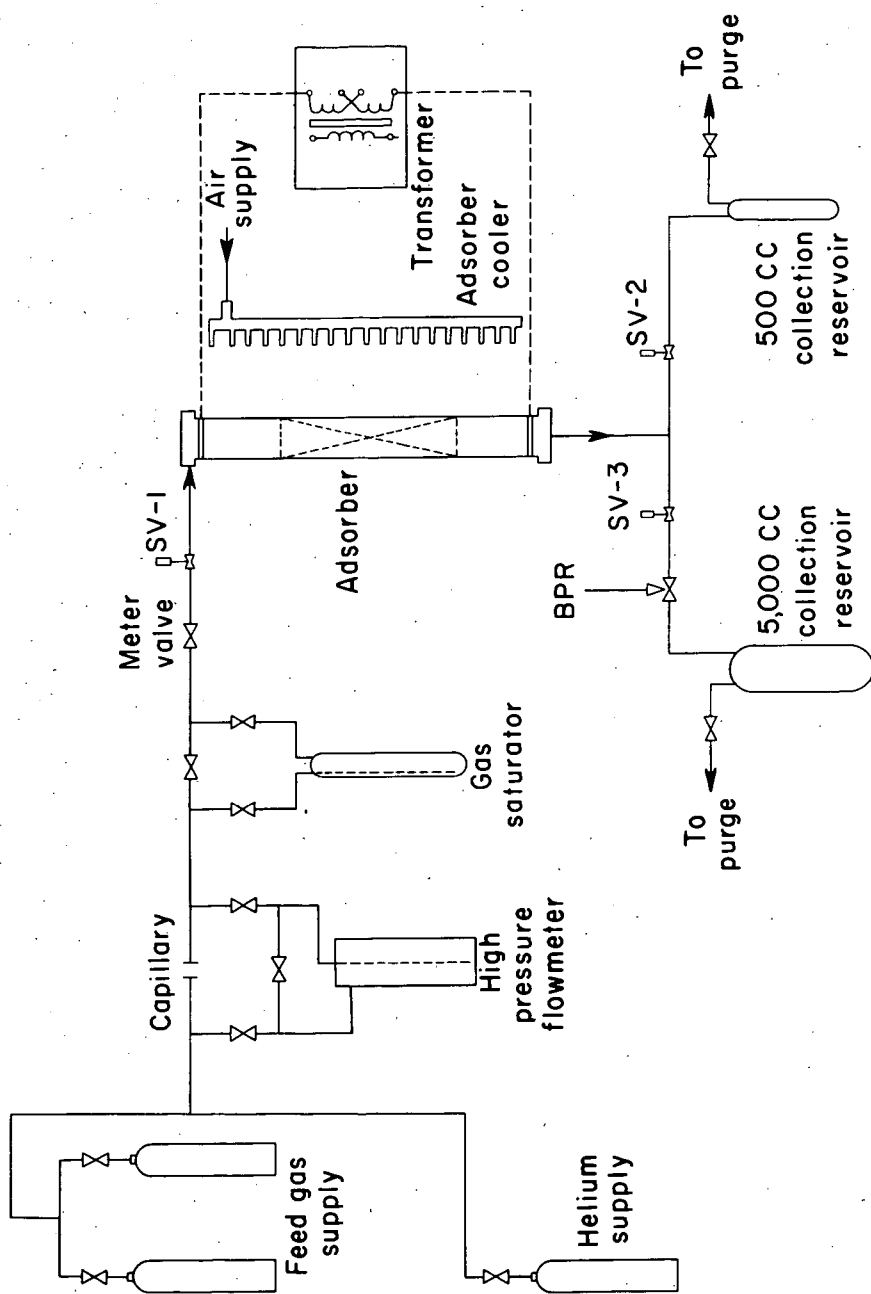Figure 1.-RAPID CYCLING, FIXED BED ABSORBER

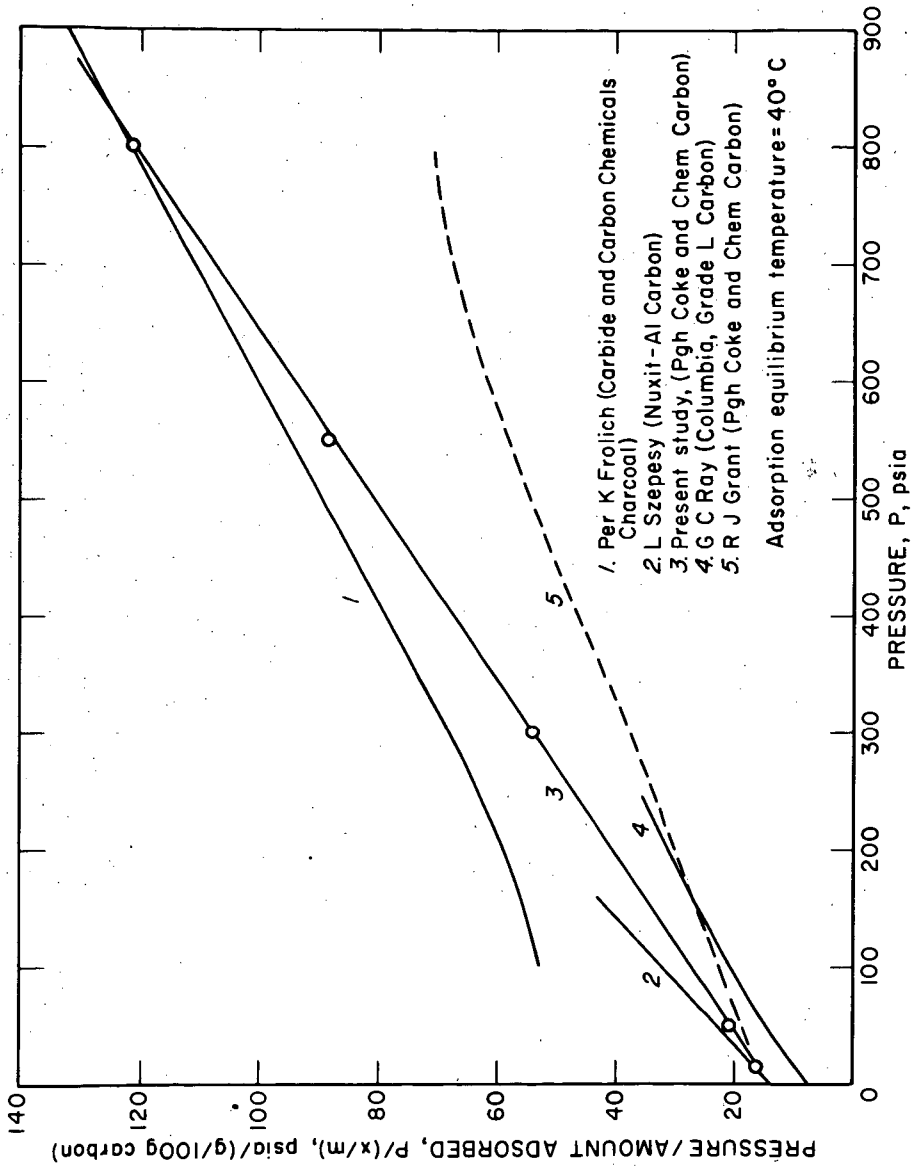Figure 2.-Overall flowsheet of bench-scale adsorption unit.

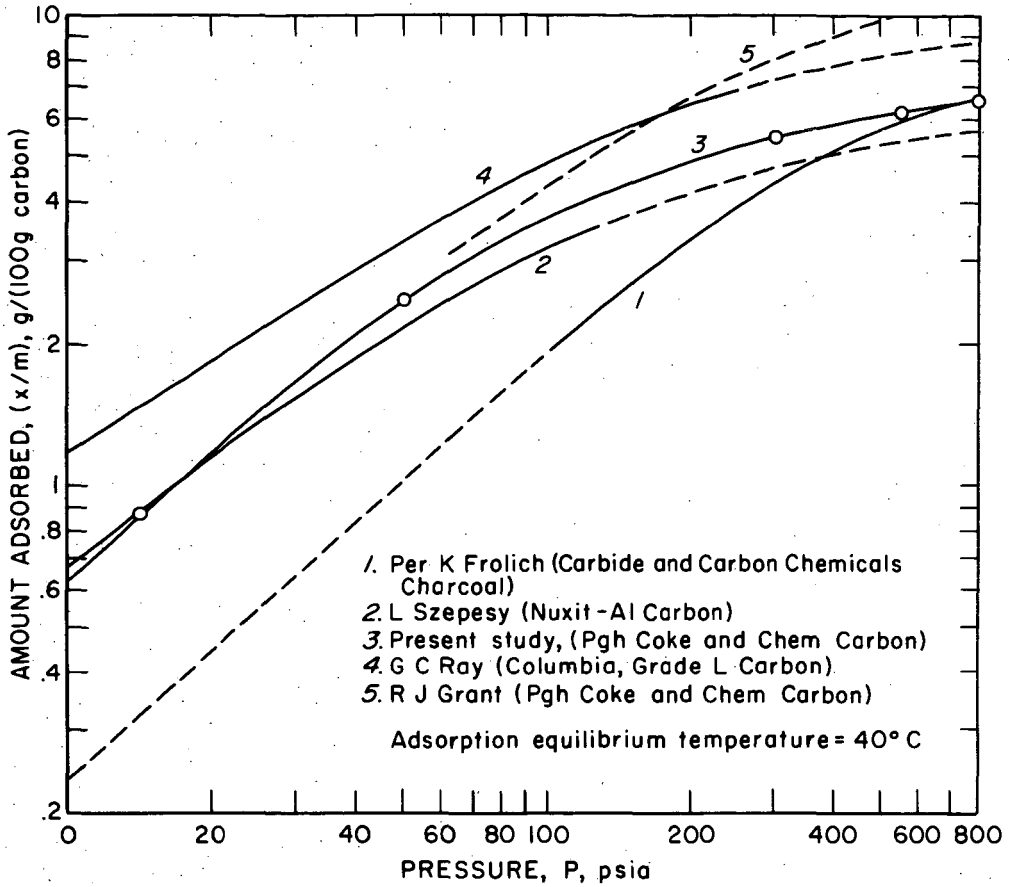Figure 3.—Adsorption isotherms for methane on various types of activated carbon, Langmuir plots.

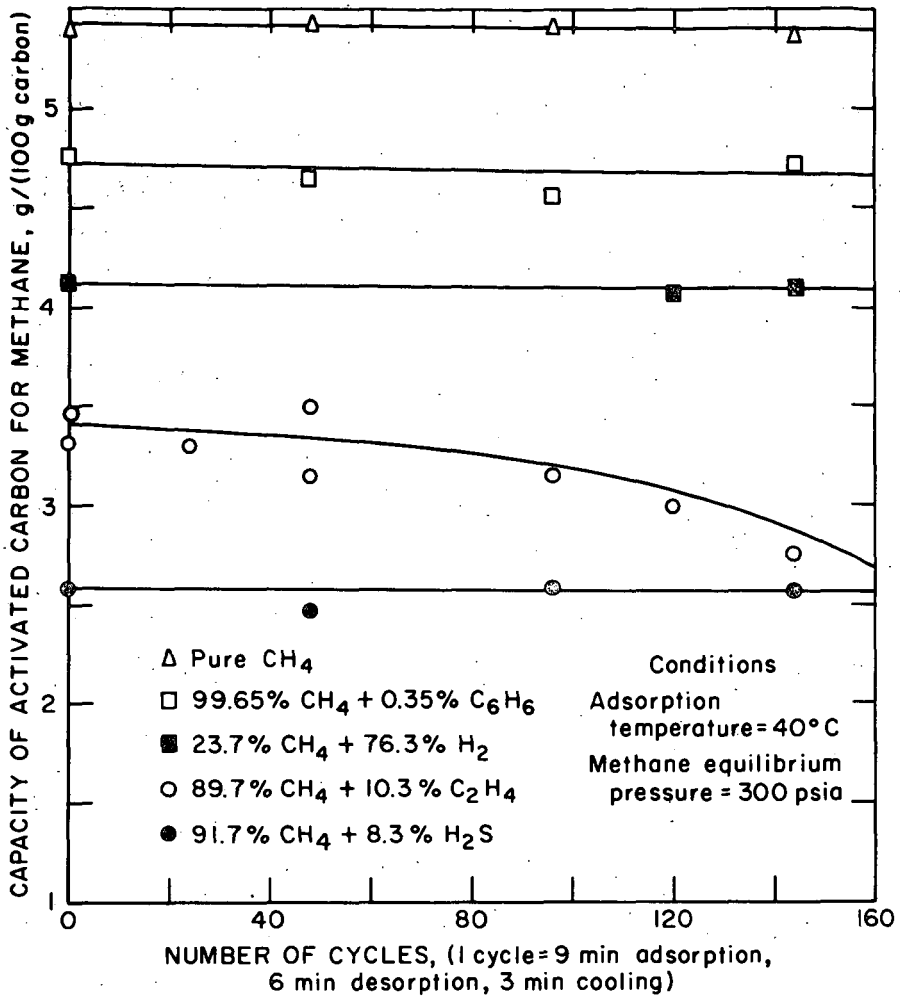Figure 4.—Adsorption isotherms for methane on various types of activated carbon, Freundlich plots.

Figure 5.—Effect of contaminating gases and repeated cycling upon activated carbon's capacity for methane.